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Page Denied

Next 1 Page(s) In Document Denied

D.V. Kokoulina and B.N. Labanov, Doklady Akad. Nauk SSSR 112, 692-695 (1957) (Paper presented to the Academy of Sciences USSR by A.N. Frumkin, 11 August 1956)

ON THE NEGATIVE DIFFERENCE EFFECT ON MAGNESIUM

For the anodic dissolution of magnesium in aqueous solutions of salts there is characteristically an increase in the evolution of hydrogen with increase of the density of the anodic current, which in the theory of corrosion is designated the negative difference effect. The negative difference effect is observed only for active, easily oxidized metals: Mg, Al, etc. (1-4). For Mg the negative effect has been described for solutions of salts, the positive for HCl solutions (5).

There are two hypotheses explaining the the negative difference effect. The first completely links the increase of the evolution of hydrogen with an increase of corrosion of the anode as a consequence of the breakdown during the anodic polarization of the oxide film protecting the metal (1,3,4,6-8). The second hypothesis connects the evolution of hydrogen only with this, that during the anodic process the metal passes into solution partly in a lower valence, for example, monovalent magnesium, and the water oxidizes the latter to the usual valence and hydrogen is evolved from the solution. During this process it is considered that self-dissolution during the polarization practically does not take place (9,10). The experimental data existing for the magnesium anode: evolution of hydrogen after switching off the current (9), direct proportionality between the rate of evolution of hydrogen and the anodic current density (7,8), equal rates of evolution of hydrogen during the passage of continuous and commutated current of low frequency (60 cycles/sec) (9), the reduction of oxidizing agents at the magnesium anode — can be explained starting from both points of view. In the existence of reduction of solutions of oxidizing agents by the flow of the anolyte into them, when there is no direct contact of the anode with the solutions of oxidizing agents, better proving the certain stability of the ion Mg^{+} in solution, it may be doubted, since the magnitude of the effect lies on the boundary of sensitivity of the method. Thus the practical material existing to the present time can not serve to prove convincingly the accuracy of one or the other of the hypotheses. In connection with this we were given the present work.

During the anodic polarization, at current densities greater than the current of self-dissolution, but less than the passivation current of magnesium in a given solution, the steady potential of the magnesium anode does not depend on the current density. However, the potential undergoes changes in time which are analogous to the changes of potential of an aluminum electrode (1). In fig. 1 are shown the changes in time during changes in the current density. The steady values of the potential at both current densities are almost equal, however, in the first moment after a change of the current density the potential of the electrode appears different from its steady value. These changes, doubtless, attest to a change of the state of the surface of the electrode: immediately after decreasing or switching off the current the surface of the magnesium, in the course of several seconds, appears more active than in the stationary state in these conditions. A question arises whether this change of the state of the surface substantially effects the overall rate of evolution of hydrogen.

We have measured the potential of the magnesium electrode and the rate of evolution of hydrogen in a solution of $MgSO_4$ during the passage of an anodic current of rectangular impulse form, during which the periods of time of passage and of interruption of the current were equal. As seen from fig. 2, the potential of the electrode undergoes significant oscillations, the amplitude of which depends on the frequency of the sequence of impulses, during which the average value about which the oscillations of potential take place lies approximately 0.15 volts more negative than the steady potential during polarization by continuous current of the same strength.

During the impulse current the anode becomes activated in the time of the passage impulse, but during the interruption of the current its passivation takes place. At high frequencies of the impulse current the surface will not have time to become completely passivated in the time of interruption of the current and completely activated in the time of passage of the current; during this the self-dissolution, generally speaking, ought not to be equal to the self-dissolution during continuous passage of current.⁺ Therefore, if the origin of the negative difference effect

⁺ For comparison of the rates it is necessary to compare the quantity of hydrogen evolved during the continuous passage of current for a definite interval of time with the quantity of hydrogen evolved during the interrupted passage of current for the second interval of time. The rates of self-dissolution can be equal during continuous and impulse passage of current only in that case when in the first moments of passage of the current in the impulse the evolution of hydrogen turns out to be as much diminished as it is increased in the first moments of the interruption of the current such that these processes mutually neutralize each other; however, such neutralization, which extends over a wide range of anodic current densities and frequencies of the impulse current, is hardly probable.

appears in the self dissolution of the anode, then the rate of evolution of hydrogen during the impulse current ought to differ from the rate of evolution during the passage of steady current of the same strength. If the origin of the evolution of hydrogen appears in the chemical reaction of oxidation of the ion Mg^{+} by water, then the rate of evolution of hydrogen will be determined only by the quantity of Mg^{+} produced in unit time, proportional to the density of the passing current, independent of the presence of the interruptions of the current and of the changes of the state of the surface.

As is seen in fig. 3, the rate of evolution of hydrogen in a solution of $MgSO_4$ appears equal during continuous and impulse passage of current, does not depend on on the frequency of the sequence of impulses and the concentration of the solution, but depends only on the density of the passing current. Although during the continuous current all of the curves exhibit nearly a constant potential -1.75 volts vs. normal calomel electrode, and show during the impulse current of various frequencies potentials with different mean values of from -1.9 to -2.0 volts vs. N.C.E., the rates of evolution of hydrogen at the anode do not depend on the potential.

We also discovered the evolution of hydrogen on magnesium when the potential of the anode was 0.4 to 0.6 Volts more positive than the equilibrium potential of hydrogen (solution of $MgSO_4$ (2 N) with addition of $K_2Cr_2O_7$ (0.5 M) at anodic current densities of 20 to 30 ma/cm²). The resistance of the electrode measured with the interruption of current amounted in these conditions to about 1 ohm/cm² and should not give significant distortions of the measured electrode potential. This result agrees with the assumption about the entry into solution of monovalent magnesium, however, considering the great heterogeneity of the surface, the fact of evolution of hydrogen at potentials more positive than the equilibrium potential can not be considered to be fully proved.

These two experimental facts; the independence of the rate of hydrogen evolution on the presence of the interruptions of the current and on the potential of the electrode can not be explained by the electrochemical process of self-dissolution of the anode, but serve to support the assumption that the elementary electrochemical act during the anodic dissolution of magnesium appears as a single electron transition with the production of the ion Mg^{+} .

We have measured the rate of evolution of hydrogen during the anodic polarization of magnesium in various solutions. The results of these measurements are presented in fig. 4. In solutions of NH_4Cl and HCl , with increase of the current density there appears at first a decrease in the rate of evolution of hydrogen (positive difference effect). During further increase in the current density a minimum rate appears. Then comes an inversion of the difference effect: from the positive, it inverts to the negative during which the value of the rate of evolution of hydrogen is near to the values observed in neutral solutions.

On the basis of our experimental data ^{W₁} think that the evolution of hydrogen at a magnesium anode is dependent on both origins: 1) the chemical reaction of oxidation of the ion Mg^+ by water, the rate of which V_1 is proportional to the rate of dissolution of magnesium and does not depend on the potential of the electrode, the concentration and composition of the solution, and 2) the reaction of self-dissolution of the anode, the rate of which V_2 depends on the potential of the electrode, the state of the surface and the composition of the solution. The overall rate of evolution of hydrogen, if changes in the state of the surface are neglected, is indicated by the equation:

$$V = V_1 + V_2 = \frac{6.95 i (2 - n_1)}{n_1} + V_0 \exp\left(\frac{-\alpha_1 \Delta\phi F}{RT}\right) \quad (1)$$

where V_0 is the rate of evolution of hydrogen without current, α_1 is a coefficient characteristic of the cationic process of evolution of hydrogen on Mg with the given state of the surface, $\Delta\phi$ is the shift of potential from the stationary value during the anodic polarization, i is the current density of the passing current in $\text{amp/cm}^2 \cdot \text{min}$.

Equation (1) approximately expresses the quantitative relations observed during the evolution of hydrogen at the magnesium anode. The first term increases, but the second decreases with increase of anodic current density $+$. Therefore the curve (V, i)

+ Decreases provided there is an increase in $\Delta\phi$. With no change in the state of the surface $\Delta\phi$ ought to increase according to the equation:

$$i = \frac{V_0}{6.95} \exp\left(\frac{\beta \Delta\phi F}{RT}\right)$$

In fact, on account of the activation of the surface, beginning with a certain current density, $\Delta\phi$ does not increase; consequently the second term appears unchanged or even increases, in so far as the activation leads to a reduction in the hydrogen overpotential.

ought to exhibit a minimum, the position of which indicates the change of sign of the difference effect from positive to negative. In neutral solutions, where the self-dissolution is small and the minimum should appear at several tenths of a milliampere per square centimeter, with all experimental current densities there appears only an increase in the rate of evolution of hydrogen, but in acid solutions, both effects.

The evolution of hydrogen at current densities significantly greater than the current density of self dissolution in each solution is practically dependent on one origin: the reaction of oxidation by water of the ion Mg^+ (or the radical MgOH), produced during the anodic polarization of magnesium. However, at with certain conditions the increase of the evolution of hydrogen is partly caused by the anodic activity of the metal, if such is possible in the given solution. The inversion of the difference effect comes about thanks to the superposition of the reactions of self-dissolution of Mg and the reaction of oxidation of the ion Mg^+ .

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NOTE SUBMITTED WITH PROOFS: At the time of printing of our work the paper of Greenblatt (11) was published on the mechanism of the anodic dissolution of Mg in solutions of NaCl. His results agree with our conclusions.

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Translation of the captions of the figures.

Fig. 1. Ordinates -- potential in volts vs. normal calomel electrode
Abscissae -- time in seconds

Caption: Changes of potential of the magnesium anode in time with changes of current density: 1--during increase from 7 to 67 mamp/cm², 2--during decrease from 67 to 7 mamp/cm². Parts a and a' correspond to the potential at current density of 7 m amp/cm²; parts b and b' -- during 67 m amp/cm². Solution MgSO₄ (1 Normal)

Fig. 2. Coordinates same as fig. 1.

Caption: Changes of potential in the process of polarization of Mg by impulse current: 1-- 1000 cycles/sec; 2-- 100 cycles/sec; 3--20 cycles/sec. Solution MgSO₄ (1 N) Current density during impulse 51.3 m amp/cm²

Fig. 3. Ordinates-- cm³/cm² min i.e. cm³ of hydrogen per cm² of electrode surface per minute.
Abscissae -- current density in amp/cm²

Caption: Rate of evolution of hydrogen in solutions of MgSO₄ as a function of the anodic current density. Polarization with continuous passage of current: a -- 1 N solution; 6 -- 0.1 N solution. Polarisation with impulse passage of current: 6 -- 1 N solution, 2 -- 0.1 N solution (10000 cycles/sec); 8 -- 1 N solution (6 cycles/sec)

Fig. 4. Coordinates same as fig. 3.

Caption: Rate of evolution of hydrogen at Mg anode as a function of the current density: a -- 1 N MgSO₄; 6 -- 4.6 N MgCl₂; 8 -- 5 N CaCl₂; 2 -- 1 N NH₄Cl; 8 -- 0.5 N NH₄Cl; e -- 0.039 N HCl; * -- 0.117 N HCl.